COLOUR REMOVAL OF RAW CARRAGEENAN BY USING SODIUM HYPOCHLORITE AS BLEACHING AGENT

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ABSTRACT

Carrageenans are natural ingredients that represent one of the major texturizing ingredients used by the food industry. However, the extracted carrageenans from seaweeds may have colour such as light brown. These criteria will affect marketed sector because the product are not presented in an interesting ways. Therefore, sodium hypochlorite is one of the effective treatment options and it has potential for removing of colour as bleaching agent. This is due to chlorine is the basis for the most common material used on bleaching. However, the availability of chlorine will give unpleasant odour to the product. This problem can be overcome by addition of sodium thiosulfate into the seaweed to neutralize the sodium hypochlorite. The purpose of this study is to remove colour of carrageenan from seaweed. Amount of sodium hypochlorite are the variable need to be controlled in order to get the optimum condition removing colour of extracted carrageenan from seaweed. When the amount of sodium hypochlorite increased, the time needed to decolourizing carrageenan become more faster. However, by using chlorine bleach (sodium hypochlorite) as a bleaching agent in food processing, this operations must follow permissible regulations to dealing with health effect.

PENYINGKIRAN WARNA KARAGENAN MENGGUNAKAN NATRIUM HIPOKLORIT SEBAGAI AGENT PELUNTUR

ABSTRAK

Karagenan merupakan bahan semulajadi yang terdiri sebagai salah satu jalinan bahan yang digunakan di dalam industri makanan. Walaubagaimanapun, pengeluaran karagenan daripada rumpai lautakan mengeluarkan warna coklat seakan cair. Faktor ini akan memberikan kesan kepada pasaran kerana ia tidak dihasilkan dalam bentuk yang menarik. Oleh itu, Natrium hipoklorit salah satu rawatan yang berkesan dan ia berpotensi untuk mengeluarkan warna kerana ia adalah bahan peluntur. Hal ini kerana klorine merupakan bahan asas yang dikenali digunakan sebagai peluntur. Tetapi kehadiran klorin memberikan kesan bau yang kurang menyenangkan kepada produk. Masalah ini dapat diatasi dengan penambahan Natrium thiosulfat kedalam rumpai laut untuk meneutralkan Natrium hipoklorit. Tujuan pembelajaran ini adalah untuk mengeluarkan warna karagenan daripada rumpai laut. Bila bilangan Natrium hipoklorit bertambah, masa yang diperlukan untuk melunturkan warna karagenan adalah singkat. Walaubagaimanapun, bila mengunakan klorin sebagai bahan peluntur di dalam pemprosesan makanan, operasi ini perlu mengikut kebenaran pertubuhan untuk mengelakkan dari memberikesan kepada kesihatan.

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LIST OF SYMBOLS

°C	Degree celcius
g	Grams
L	Litre
mL	Millilitre
min	Minutes
s	Seconds
%	Percentage

LIST OF ABBREVIATIONS

ABS	Absorbance
FTIR	Fourier transform infrared spectroscopy
HCl	Hydrochloric acid
KOH	Potassium hydroxide
NaOCl	Sodium hypochlorite
$Na_2S_2O_3$	Sodium thiosulfate
UV-Vis	UV-Vis specphotometer

CHAPTER 1

INTRODUCTION

1.1 Introduction

Carrageenan is natural ingredients has been used in food application for decades and are generally regarded as safe (GRAS) (Pereira *et al.,* 2009). It has been used in food industry for additive, thickening, gelling agent and new application of carrageenan in the food industry are in pill and tablets (Distantina *et al.,* 2011).In addition, carrageenan is the third most fundamental hydrocolloid in the world after starch and gelatin (Mustapha *et al.,* 2011). Carrageenan is the main structure of the seaweed which is located in the cell wall and intracellular matrix of the plant tissue (Christopher *et al.,* 1998).

Seaweed can be classified into three basic type of colour which is brown (Phaeophyta), red (Rhodophyta) and green (Chlorophyta) seaweed. The red seaweed from kappa carrageenan types is used on this research because it is able to form rigid

gels. The red colour of the Rhodophyta (red seaweed) is comes from the present of pigment phycoerythrin which reflects red light and absorb blue light (Hashim and Chu, 2004).

In this research, sodium hypochlorite is selected as bleaching agents due to their special functional properties. When used properly, chlorine bleach such as sodium hypochlorite is the most active chemical to kills the undesirable microorganism. This is due to the fact that, chlorination is widely used in water disinfection and also an effective method chlorinating agent since the beginning 20^{th} century. Furthermore, chlorine and sodium hypochlorite was economic disinfectants to be used for bleaching of seaweed.

1.2 History of Carrageenan

In Ireland, carrageenan was found by a British pharmacist Stanford in 1810 who extracted it from Irish Moss (Chondrus crispus). Then, the name for the extracted seaweed is given as ‘carrageen’ introduced around 1829. The name was changed to carrageenan so as to meet with the ‘-an’ suffix for the name of polysaccharides. The application of Irish Moss was spreading to New England and USA due to migrants fleeing the potato famines of the 18^{th} and 19^{th} centuries. During World War II, a small processing carrageenan occurs in Ireland, New England and

USA because the lack of agar supply from Japan. After the war finished, carrageenan became a major force in the food-additives business and is now the leading seaweed-extract on the worlds markets (The Seaweed Site Website).

Carrageenans represent one of the major texturizing ingredients used by the food industry. Besides carrageenan being used in food industry, agar is the first colloid to be industrialized and it has the same purpose as a gelling agent for food besides as an inert support medium for microbial culture. The traditional process for the production of carrageenan is the alcohol precipitation process. This method was able to produce any type of seaweed as well as produce any type of carrageenan. However, the cost involves in this process is very high. Due to this reason, alcohol precipitation becomes less favourable in the production of carrageenan (CyberColloids Website).

1.3 Problem Statement

Carrageenans are one of other types gelling agent use in food industry. It can be obtained by extraction from seaweed. However, after the extraction,the solution may have unpleasant odour and colour such as light-brown colour. These criteria will affect the marketed sector because the products are not presented in an interesting ways. Therefore, sodium hypochlorite is act as bleaching agents to remove the colour of the carrageenan. However, sodium hypochlorite has smelled of chlorine odour on

the final product. This odour could be overcome by neutralizing the free chlorine with sodium thiosulphate (Kalinowski, 2009).

According to Warburton, the exposure free chlorine gas will cause health effect to the workers. Chlorine has distinct odour that harmful if inhaled, will cause respiratory tract burns, skin burns and eye burns. Beside that, the chlorine gas produced during bleaching process tends to environment pollution. Thus, an environment eco-friendly bleaching of seaweed is required on further research (Haiyan, 2008).

1.4 Objectives

The objectives of this research are

(1) to investigate the effectiveness of sodium hypochlorite as bleaching agent from seaweed.
(2) to study odour removal of free chlorine by using sodium thiosulfate from seaweed.
(3) to produce raw carrageenan with better appearance, low colour and free from unpleasant odour.

1.5 Scope of Study

In order to achieve the objective stated above, the scopes of study in this research are:

(1) to investigate the efficiency of sodium hypochlorite as the bleaching agent with different concentration which is 0, 0.1, 0.2, 0.3 and 0.4 percent of sodium hypochlorite.

(2) to investigate the efficiency of sodium thiosulphate as odour removal of free chlorine with different concentration which is 0, 0.1, 0.2, 0.3 and 0.4 percent sodium thiosulfate.

(3) to determine the effectiveness of sodium hypochlorite with time which is 0 minutes, 15 minutes, 30 minutes, 45 minutes and 60 minutes.

(4) to study the effect of temperature on bleaching which is $22^{O}C$ (room temperature), $30^{O}C$ and $35^{O}C$, $40^{O}C$ and $45\ ^{O}C$

1.6 Rational and Significant

The main purpose of this study is to remove the odour and colour from the raw carrageenan using sodium hypochlorite as bleaching agents. The bleaching agent used in this research was sodium hypochlorite. This is because sodium hypochlorite is able to bleach the seaweed colour. In addition, it is also the best example of chlorine compound that used as disinfectant which is can kills the living microorganisms on the substance (Woo Byun *et al.*, 2006).

Further seaweed processing is required to remove the odour of free chlorine on the seaweed. This chlorine can be overcome by the addition of sodium thiosulfate into the seaweed. This is because sodium thiosulfate is neutralizing agent for the sodium hypochlorite. In medical application, sodium thiosulfate is used for medical therapies as an antidote in the treatment of cyanide toxicity and to avoid ototoxicity in carboplatin recipients (Chetan Vedvyas, 2012).

CHAPTER 2

LITERATURE REVIEW

2.1 Types of Carrageenan

There are many types of carrageenan, it can be identify by their properties and chemical structure. However, the type of carrageenan usually used in food industry comprises of mixture from a lot of species red algae depends on industrial needed (Molecular Gastronomy Network Website). The carrageenan family has three main branches types as kappa (k-), iota (i-) and lambda carrageenan by the number (one, two or three) of sulphate groups per repeat unit of disaccharides (Yuguchi *et al*., 2003).

2.1.1 Iota Carrageenan

Iota carrageenan is thermoreversible gels. It has high molecular weight linear polymer consisting principally of an alternating sequence of 3-linked β-d-galactose 4-sulfate and 4-linked 3,6-anhydro-β-d-galactose 2 sulfate (Ozbek and Pekcan, 2006). The iota carrageenan is predominantly gets from *Eucheuma Spinosum* and *Ahnfeltia concinna.* The iota carrageenan is a gelling agent that especially elastic and flexible in the present of calcium ions (Totalingredients.net Website). On the other hand, carrageenan gels made from iota product are flaccid and compliant (Christopher *et al*, 1998). Figure 2.1 below depicts the structure of iota carrageenan.

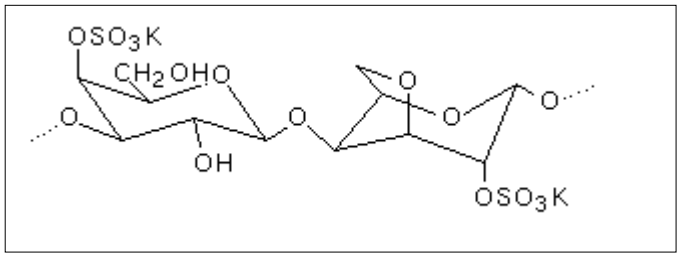

Figure 2.1 Structure of iota carrageenan.

2.1.2 Lambda Carrageenan

It's has structure is based on alternating chain of O-2-sulfated-β-d-galactose-(1→4)-O-2,6-disulfated-α-d-galactose units (Zhou *et al.*, 2006). The lambda carrageenan is produced from the extraction of the *Gigarginacaea* and *Phyllophoracaea* types of red algae. Lambda carrageenan is non-gelling type and forming thick viscous solution (Mustapha *et al.*, 2011). In food application, lambda carrageenans provide an instant smooth and creamy texture. Lambda carrageenan is protein reactive and can be used for soy protein and dairy product purpose (Gum Technology Website). Figure 2.2 below depicts the structure of lambda carrageenan.

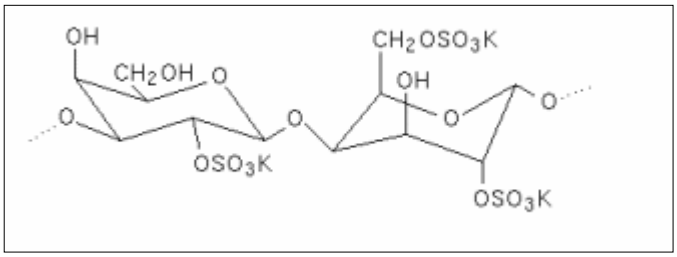

Figure 2.2 Structure of lambda carrageenan.

2.1.3 Kappa Carrageenan

The kappa-carrageenan is linear water soluble polysaccharides extracted from a lot of type of marine red algae with the main structure on an alternating disaccharide repeating unit of a-(1-3)-d-galactose-4-sulphate and h-(1-4) 3,6-anydro-d-galactose (Magione, 2005). It is the commonly used type of carrageenan. This type of carrageenan is used as gelling agent. In the presence of potassium ions, the carrageenan becomes firm and elastic gels. On the other hand, it will become stiff and brittle texture in the presence of calcium ions.

Kappa carrageenan is thermo-reversible means it melts when heated and becomes gels during cooling (Totalingredients.net Website). It has the ability to form gels on cooling hot solution between 40^{O}C and 60^{O}C. It is depends on the amount of cation present on the solution. Kappa-carrageenan is thermally reversible and will be re-gels on cooling. Beside that, it will melt by heating 5 to 20^{O}C above the gelling temperature which is between 65 into 80^{O}C (FMC Corporation (UK) Ltd). Figure 2.3 below depict the structure of kappa carrageenan.

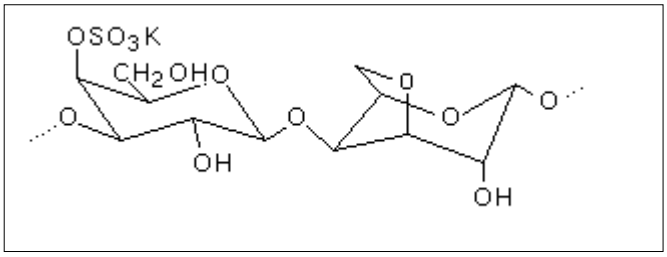

Figure 2.3 Structure of kappa carrageenan.

Carrageenan can be obtained within the cell wall and intracellular matrix of the plant tissue. The percentage of carrageenan content on the seaweed is about 30% to 80% based on seaweed dry weight (Tsai *et al.*, 2010). Kappa-carrageenan can form strong gel make it useful for dairy product. Kappa-carrageenan can be obtained from *Eucheuma cottonii* that produce higher gel strength and more brittle than the kappa from *Chondrus crispus* or *Gigartina sp* (Bost *et al*, 2002).

This seaweed type (kappa-carrageenan) is the largest production worldwide. Nowadays, the *Eucheuma cottonii* is the most important commercial seaweed for carrageenan production (Qhairul Izzreen and Ratnam, 2011). There are no nutritional provided by carrageenan to human body because it cannot be digested. Carrageenan used in food industry because its functional properties that can be used to control moisture, texture and to stabilize food (Mishra *et al.*, 2006). The yield and functional properties of carrageenan such as gel strength contribute its value to food industry (Distantina *et al.*, 2011).

2.1.4 Difference Between Kappa, Iota and Lambda Carrageenan

From an observation, kappa carrageenan and iota carrageenan almost have the same alternating sequence of disaccharide repeat units. The different only on the presence of iota or absence of kappa of the sulphate group on the 2 position of the 4-linked galactopyranosyl unit. Kappa has one negatively charged sulphate groups per every disaccharide repeating unit whereas iota carrageenan have only one. Therefore, kappa-carrageenan with one negative charged sulphate groups shows selectivity for monovalent potassium ions while the iota carrageenan that has two sulphate groups prefers divalent calcium ions. Other research shows, lambda carrageenan that has three negative charged sulphate group prefer with iron (III) ions (Running *et al.,* 2011).

2.2 Bleaching Agent

Bleaching agents are the compound widely used indairy products or industrial purposes. This is due to the fact that, bleaching agents is able to lighten or remove the colour of the compound in order to get the specific needs. Clorox is the example of bleaching agents was very popular real laundry bleach on the market. Bleaching agents also can be used for laundry detergents to remove the dirt at the clothes. In addition, it can be used as clean and sterilize objects and surface. There are twotypes